REDUCTIVE DEHALOGENATION OF TRICHLOROETHENE MEDIATED BY WETLAND DOC-TRANSITION METAL COMPLEXES

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ABSTRACT: Natural attenuation of chlorinated solvents, such as trichloroethene (TCE), within aquifers is often slow, leading to long contaminant plumes which can reach surface water discharge points such as wetlands. Though suboxic environments, such as high organic carbon wetland sediments, are often sufficiently reducing to make reductive dechlorination reactions thermodynamically favorable, the transfer of electrons from reduced species to a chlorinated solvent is often kinetically constrained. The reduction rate may be enhanced in the presence of compounds capable of facilitating the transfer of electrons from a bulk reductant to the chlorinated solvent of interest. Ni and Cu complexes with dissolved organic carbon (DOC) in wetland sediment porewaters and surface water were able to mediate the reductive dehalogenation of TCE using Ti(III) citrate as the bulk reductant. The reactions were pseuo-first-order with half lives typically less than 2 h. Reaction rates were comparable for systems containing Ni or Cu Aldrich humic acid complexes. Dechlorination was complete, with the dominant products being ethene and ethane. The mass balance was near 100% and chlorinated intermediates were either absent or at extremely low concentrations.

INTRODUCTION

Trichloroethylene (TCE) is commonly used as a solvent in commercial and industrial processes. Prior to the adoption of current regulatory protocols, commonly accepted handling and disposal practices have resulted in widespread groundwater contamination (Bourg et al., 1993). TCE has been classified as a priority groundwater pollutant by the U.S. Environmental Protection Agency and is of particular concern because under anoxic conditions it can be reduced to vinyl chloride, a known carcinogen.

Natural attenuation of chlorinated solvents within aquifers is often slow, leading to long plumes which can reach surface water discharge points such as wetlands. Though suboxic environments, such as high organic carbon wetland sediments, are often sufficiently reducing to make reductive dechlorination reactions thermodynamically favorable, the transfer of electrons from reduced species to a chlorinated solvent is often kinetically constrained. In the presence of compounds which can act as electron mediators, such as the transition metal organocomplexes vitamin B_{12} (Co), coenzyme F_{430} (Ni), and hematin (Fe), the reaction rates can be greatly enhanced (Gantzer and Wackett, 1991).

Humic substances are a class of naturally occurring organic polyelectrolytes produced primarily during the degradation of plant materials. They are present in both aquatic and terrestrial environments and have been shown to complex or bind with a wide range of organic and inorganic pollutants

including transition metals. Ni- and Cu-Aldrich humic acid complexes have. recently been shown to be effective electron mediators for the reductive dechlorination of TCE (O'Loughlin et al., 1999). Humic substances (humic and fulvic acids) are particularly abundant in wetland environments, typically comprising up to 70 - 90% of the dissolved organic carbon (DOC) on a mole C basis (Thurman, 1985). In the present work, experiments were conducted to determine if Ni or Cu complexes with DOC from wetland sediment porewaters and surface waters could mediate the reductive dechlorination of TCE.

MATERIALS AND METHODS

Site Description. Water samples were collected from three distinct wetland environments which were located in Aberdeen Proving Ground (APG), Maryland; Collier Mills Wildlife Management Area (CMWMA), New Jersey; and Tyndall Air Force Base (TAFB), Florida.

The APG site is a tidal freshwater marsh located adjacent to West Branch Canal Creek with vegetation consisting mainly of a monotypic stand of common reed (*Phragmites australis*). A detailed description of the site has been made by Lorah et al. (1997). Groundwater was collected from the OC rich upper peat unit at a depth of approximately 1 m.

The CMWMA site is a mixed hardwood swamp bordering the Elisha Branch of the Toms River. At the time of collection the area was under extreme drought conditions and there was no standing water. Groundwater was collected by removing surface material to a depth of approximately 0.3 m and sampling from the water which seeped into the depression.

The TAFB site is a seasonally flooded mesic/wet slash pine (*Pinus elliottii*) flatwood located in a stable dune zone along the Gulf Coast of the Florida Panhandle. Surface waters were collected from a stream draining the site shortly (<6 h) after a major precipitation event (>5 cm).

Experimental Setup. The APG and CMWMA porewaters were centrifuged to remove bulk particulates, and the supernatants and TAFB surface water were filtered through 0.22 mm nylon membrane filters. Aldrich humic acid (AHA) was treated extensively to remove residual fulvic acids and inorganic impurities including metals (Schnitzer, 1982). The DOC content of the wetland water samples and AHA solution was measured with a Shimadzu TOC-5000A Total Organic Carbon Analyzer. Within the context of this report, DOC will refer to AHA and to the solution phase OC present in the wetland water samples after filtration, and does not include OC introduced into the experimental system from the addition of reagents. Prior to use the solutions were deoxygenated by sparging with Ar for > 1 h and stored in an atmosphere of 4-6% H_2 (bal N_2). Titanium(III) citrate (250 mM) was prepared in a glovebox under anoxic conditions using a modified version of the method described by Smith and Woods (1994 #784). Briefly, 7.35 g trisodium citrate and 4.0 g Trizma® base (Sigma Chemical CO, St Louis, MO) were dissolved in 25 mL deoxygenated Milli-Q water. The solution was placed in an ice bath with continuous stirring, and 15 mL 15% $TiCl_3$ in HCl

(Fluka Chemie AG. Milwaukee, WI) was added followed by 3.2 mL 50% NaOH (w/w) to raise the pH to ~8.0 at 25 °C.

The experimental system consisted of 160 mL serum vials each containing 90 mL of aqueous phase consisting of AHA solution, wetland water, or Milli-Q water (for controls without added DOC). The solutions were spiked with 1.0 mL of 10 mM Ni^{2+} or Cu^{2+} in 0.1 M HCl (or 1.0 mL of 0.1 M HCl for controls without added metal) and 0.1 mL 1 M NaOH. After 24 h, 3 mL of 2.0 M Tris and 6 mL 250 mM Ti(III) citrate were added and the vials sealed with aluminum crimp caps with Teflon-lined rubber septa. The E_h of systems containing Ti(III) citrate was approx. -700 mV as measured with a Pt redox electrode. Vials were spiked with 5 µL of a 1.0 M methanolic solution of n-heptane (added as an internal standard). Reactions were initiated by spiking with 5 µL of a 1.0 M methanolic solution of TCE. Experimental systems were prepared in duplicate. Initial solution concentrations were 10.4, 13.4, 11.5, and 30.7 mg OC L^{-1} for AHA, CMWMA, APG, and TAFB DOC respectively, 100 mM Ni^{2+} or Cu^{2+}, 100mM Tris, and 15 mM Ti(III) citrate; the total mass of TCE in each vial was 5 µmol, with 80% partitioned in the aqueous phase. The bottles were placed on a roller drum and rotated vertically as the bottle axis remained horizontal and maintained at 20 °C in the dark. All preparative work was performed in an anaerobic glovebox with an atmosphere of 4-6% H$_2$ (bal N$_2$), or under continuous Ar sparging.

At selected intervals, 100 µL headspace samples were removed from the reaction bottles for analysis using a Hewlett-Packard 5890 Series II gas chromatograph with a GSQ column (0.53 mm id by 30 m) and a flame ionization detector (240 °C). The oven temperature program was 50 °C for 2 min, ramp 25 °C min^{-1} to 200 °C, and hold for 12 min. The system was calibrated by equilibrating known masses of analytes and internal standard (n-heptane) in serum vials containing the same ratio of aqueous phase to vapor phase as the experimental systems, thus accounting for water-vapor partitioning and allowing analyte concentrations to be expressed on a mass per bottle basis. Vapor/liquid exchange in these systems was rapid (90% of equilibrium is reached within 5 min) relative to the reaction kinetics. The identities of reaction products and intermediates were confirmed by GC/MS using a Hewlett-Packard 5890 Series II gas chromatograph with a 5971 mass selective detector. The oven temperature program was 40 °C for 3 min, ramp 25 °C min^{-1} to 200 °C, and hold for 14 min. Detector temperature was 280 °C.

Kinetic Analysis. Apparent pseudo-first-order rate constants (k_{obs}) were obtained by fitting the data for mass of TCE in the system over time to the exponential decay expression:

$$M_{TCE_t} = M_{TCE_0} e^{-k_{obs} t}$$

where t refers to time, and M_{TCE_t} and M_{TCE_0} refer to the mass of TCE in the system at times t and zero respectively. Assuming the reaction takes place in the

solution phase only, the apparent pseudo-first-order rate constant that pertains to the reaction of a volatile constituent capable of rapid partitioning between the solution phase and the headspace (k_{obs}) is related to the rate constant that would be obtained in a headspace-free system (k'_{obs}) as described by Burris et al. (1996). In this experimental system, and using a value of 0.299 mol L^{-1}_{air} mol^{-1} L_{water} (Gossett, 1987) for the "dimensionless" Henry's Law constant, the difference between k_{obs} and k'_{obs} for TCE is less than 20%.

RESULTS AND DISCUSSION

The reduction of TCE in systems containing porewater from the APG site and Ni or Cu is shown in Figure 1; similar results were observed with water from
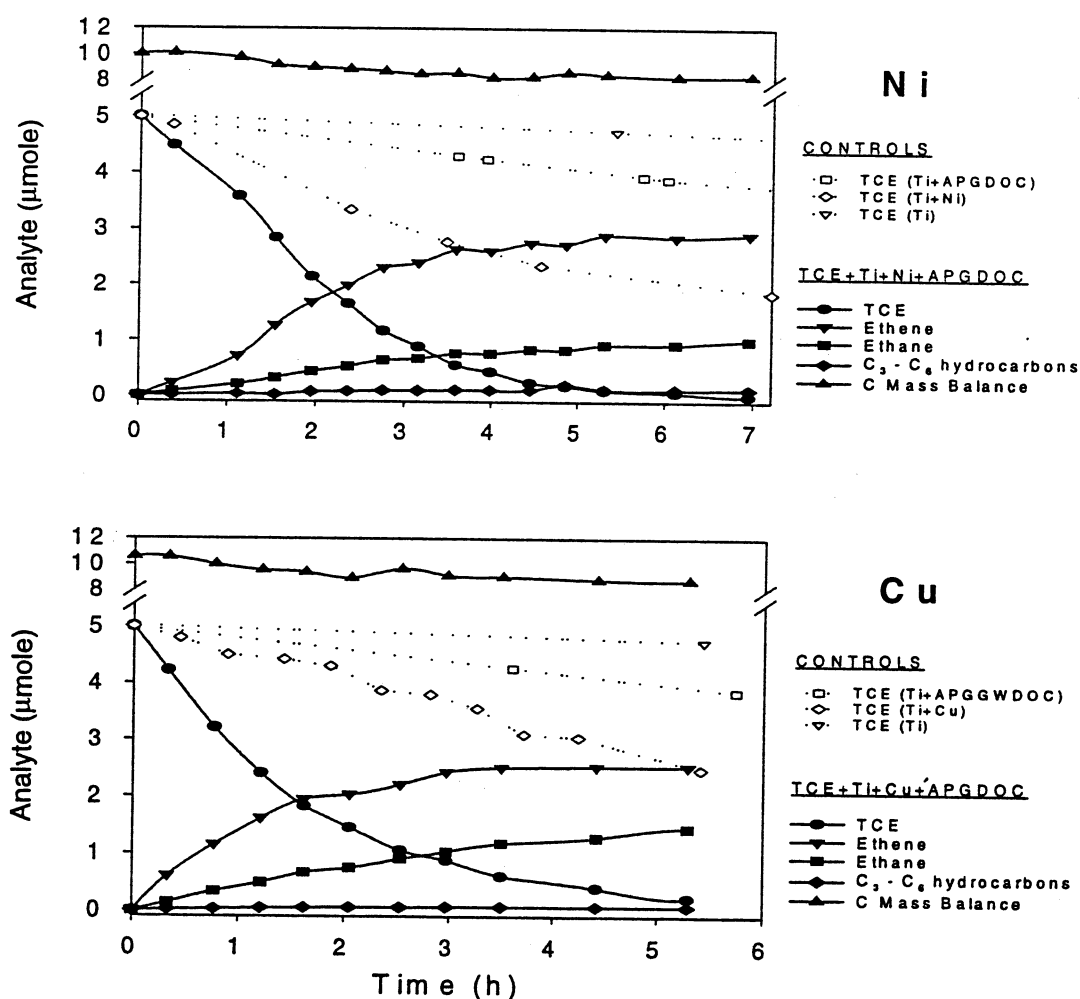
FIGURE 1. Ni- and Cu-APG DOC mediated reduction of TCE in solution containing 5 µmol TCE, 11.5 mg DOC L^{-1}, 100 µ*M* Ni^{2+} or Cu^{2+}, 100 m*M* Tris, and 15 m*M* Ti(III) citrate as the bulk reductant at 20 °C. Carbon mass balance pertains to TCE and identified reduction products only. Plots are of data from duplicate vials.

the CMWMA and TAFB sites (data not shown). TCE reduction was rapid in systems containing Ni or Cu and DOC, with > 95% loss in under 6 h. The extent of TCE reduction was substantially reduced in the absence of either Ni/Cu or DOC. While Ti(III) is a strong reductant, in the absence of an effective electron mediator it is essentially non-reactive over the time scale of these experiments. DOC and humic materials have been shown to be effective electron mediators in the reduction of nitroaromatic compounds, hexachloroethane, and carbon tetrachloride (Dunnivant and Schwarzenbach, 1992; Curtis and Reinhard, 1994). However, AHA alone (i.e. without the addition of Ni or Cu) is not an effective electron mediator for the reductive dechlorination of TCE (O'Loughlin et al., 1999), which suggests that the relatively minor reduction of TCE in systems containing DOC but without added Ni or Cu is the result of native DOC-metal complexes or other suitable mediators.

Reductive dechlorination of TCE has been extensively studied and has been shown to proceed via a combination of hydrogenolysis and β-elimination reactions producing a series of lesser chlorinated intermediates (Figure 2), including vinyl chloride, a known carcinogen. In systems containing Ni or Cu and APG DOC (as well as for CMWMA and TAFB DOC (data not shown)), TCE was rapidly reduced to ethene and ethane (Figure 1). *Cis* and *trans*-1,2-dichloroethene (DCE), 11-DCE, vinyl chloride, and acetylene were labile intermediates which typically accumulated in low yields and at no time accounted for more than 2% of the initial TCE mass on a mole C basis. In addition to ethene and ethane, additional non-chlorinated hydrocarbons were identified as terminal reaction products including methane, propene,

FIGURE 2. Potential pathways, intermediates, and end products of TCE reductive dechlorination.

propane, 1-butene, *cis-* and *trans*-2-butene, *n*-butane, and various C_5 and C_6 alkenes and alkanes. These products were observed only if TCE was added to the system and are not derived from other carbon sources. The initial step in the reductive dechlorination of chlorinated aliphatic hydrocarbons by transition metal complexes is the formation of an alkyl radical (Vogel et al., 1987). The production of hydrocarbon products containing more than two C atoms (i.e. C_3 to
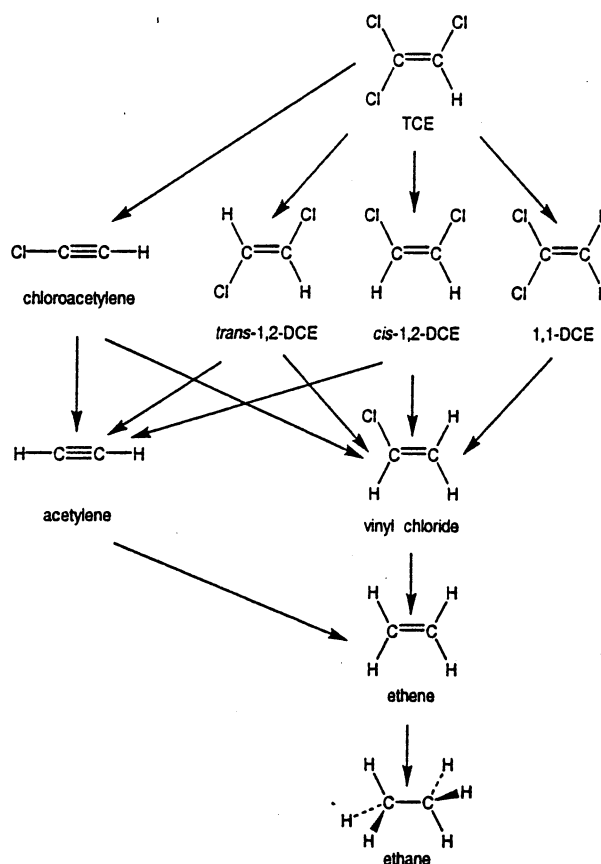
C_6) products suggests that TCE reduction mediated by Ni- and Cu-DOC complexes also involves the formation of radical intermediates. Hydrocarbon products, of which ethene and ethane comprise > 95% on a mole C basis, account for more than 90% of the C added as TCE. However, the < 10% that is unaccounted for suggests the possibility of unidentified products (losses of volatile compounds from the sealed vials were negligible over the time scale of these experiments). The overall extent of reaction and product distributions in the DOC amended systems parallel the results reported by O'Loughlin et al. (1999) for the Ni- and Cu-AHA complex mediated reduction of TCE.

The disappearance of TCE in the experimental systems was well described by pseudo-first-order kinetics and solution phase apparent pseudo-first-order rate constants are given in Table 1. The rate of TCE reduction was increased by a factor of 10 to 65 in systems containing Ni and DOC and by a factor of 13 to 25 with Cu and DOC; relative to the control containing Ti(III) citrate alone. For a given DOC source, the reaction rates for Ni and Cu amended systems were within a factor of two.

TABLE 1. Solution phase apparent pseudo-first-order rate constants for the reductive dechlorination of TCE mediated by Ni/Cu-wetland DOC complexes

Experimental System	k'_{obs} [a] (h^{-1})	adj. r^2	$t_{1/2}$ (h)
Aldrich Humic Acid			
Ni + Ti + AHA	2.28 ± 0.17 [b]	0.950	0.304
Cu + Ti + AHA	0.892 ± 0.079	0.985	0.777
Ti + AHA	0.0302 ± 0.0006	0.998	23.0
Aberdeen Proving Ground DOC			
Ni + Ti + APG-DOC	0.867 ± 0.036	0.981	0.799
Cu + Ti + APG-DOC	0.834 ± 0.027	0.989	0.831
Ti + APG-DOC	0.0495 ± 0.0004	0.999	14.0
Tyndall AFB DOC			
Ni + Ti + TAFB-DOC	0.819 ± 0.095	0.896	0.847
Cu + Ti + TAFB-DOC	0.467 ± 0.069	0.723	1.48
Ti + TAFB-DOC	0.0100 ± 0.0005	0.983	69.1
Collier Mills Wildlife Management Area DOC			
Ni + Ti + CMWMA-DOC	0.328 ± 0.010	0.986	2.11
Cu + Ti + CMWMA-DOC	0.653 ± 0.051	0.970	1.06
Ti + CMWMA-DOC	0.00719 ± 0.0004	0.982	96.3
Controls			
Ni + Ti	0.142 ± 0.014	0.949	4.86
Cu + Ti	0.170 ± 0.010	0.946	4.08
Ti	0.0338 ± 0.0032	0.949	20.5

[a] Solution phase apparent pseudo-first-order rate constant; [b] ± standard error

While the rate of TCE reduction was highest in the systems containing both Ni or Cu and DOC, TCE reduction in the controls containing Ni or Cu, but without DOC, was enhanced relative to Ti(III) citrate alone. The solution phase in all of the treatments contained Tris buffer and citrate, both of which form complexes with Ni and Cu. These complexes, or the hydrated metal ions, may also act as electron mediators in the reductive dechlorination of TCE; though not as effectively as DOC complexes.

The variability in TCE reduction by Ni-and Cu-DOC complexes was relatively low and was not accounted for by differences in the amount of DOC in the source waters examined (Figure 3). The wetland waters used in these experiments came from very distinct environments and thus there are differences in the composition of the DOC. The variability in TCE reduction rates may be due to differences in the nature of the DOC, perhaps reflecting differences in Ni and Cu complexation. The similarity in TCE reduction rates between the wetland DOC systems and AHA, suggests that the humic fraction of the DOC pool (humic and fulvic acids typically comprise 70 to 90% of the DOC in wetland waters (Thurman, 1985)) complexes with Ni and Cu, and it is primarily those complexes that serve as electron transport mediators.
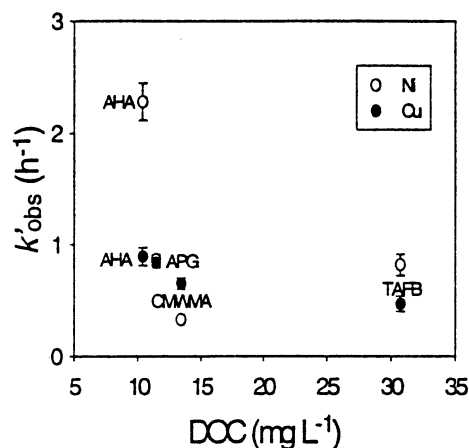

FIGURE 3. Relationship between apparent pseudo-first-order rate constants and DOC content. Error bars represent one standard deviation.

CONCLUSIONS

Our results suggest that humic–metal complexes may act as electron transport mediators in redox reactions in natural environments. Though Ti(III) citrate is not representative of "bulk" reducing agents in typical wetland environments, many wetland sediments are sufficiently reducing for reductive dehalogenation reactions to occur (as well as for reductive transformations of other contaminants of concern). Research is currently underway to determine the extent to which humic-metal complexes can mediate the reduction reactions of other compounds of environmental concern as well as to determine the ability of environmentally relevant bulk reductants to drive these reactions.

ACKNOWLEDGMENTS

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